of 78 mmol of H_2 was accumulated, and this was pumped out through a series of traps at −196 °C. The condensable material in the −196 °C traps was recondensed in the reactor, and 2-butyne (180 mmol) and triethylamine (67 mmol) were added in 15-mmol and 5-mmol increments, respectively, over a 6-day period with intervals of ~12 h between successive additions, during which the mixture was stirred at 0 °C. After all reagents had been introduced, the mixture was maintained at 0 °C for 1 day, after which the volatiles were fractionated as in the B_5H_9–$(C_2H_5)_3N$–$C_2(CH_3)_2$ reaction described above, to give 1.41 g (13.6 mmol, 20.3% yield based on amine employed) of 2,3-$(CH_3)_2$-2,3-$C_2B_4H_6$. This material had exceptionally high purity as shown by gas phase IR analysis and was easily separated from all other materials by fractionation through traps at −30 °C (which retained $(C_2H_5)_3N{\cdot}BH_3$ and a trace of 3,4-dimethyl-2-hexene, C_8H_{16}), −63 °C (which retained the carborane), and −196 °C (in which unreacted 2-butyne was collected).

As in several of the carborane syntheses described above, the time required for this procedure can be reduced significantly, at the cost of some reduction in yield. Thus, addition of the amine and alkyne in a single step (rather than incremental) followed by stirring for 3 days at room temperature gave a 16.2% yield of the carborane.

Acknowledgment. This work was supported by the Office of Naval Research.

Registry No. 2,3-$(CH_3)_2C_2B_4H_6$, 20741-68-8; 2-C_6H_5-2,3-$C_2B_4H_7$, 12080-12-5; 2-CH_3-2,3-$C_2B_4H_7$, 34228-46-1; 2-*sec*-C_4H_9-B_5H_8, 71672-52-1; $(C_2H_5)_3N{\cdot}BH_3$, 1722-26-5; $(CH_3)_2S{\cdot}BH_3$, 13292-87-0; B_5H_9, 19624-22-7; $(C_2H_5)_4N^+B_3H_8^-$, 12555-74-7; $C_2(CH_3)_2$, 503-17-3; C_6H_5-C_2H, 536-74-3; CH_3C_2H, 74-99-7; $(C_2H_5)_3N$, 121-44-8; $(CH_3)_2S$, 75-18-3.

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B-Halogenation of Ammonia–Borane: A Nuclear Magnetic Resonance Study

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Received June 11, 1979

Ammonia–borane and BX_3 (X = F, Cl, Br) were combined at low temperature in molar ratios from 3:1 to 1:2 with ether solvents. After warming and stirring of the mixtures at 25 °C for 18 h, NMR samples were taken of each reaction mixture. The ^{11}B spectra of products from the $H_3N{\cdot}BH_3$–BCl_3 reactions gave evidence for the new compounds $H_3N{\cdot}BH_2Cl$ and $H_3N{\cdot}BHCl_2$ along with $H_3N{\cdot}BCl_3$, $(C_2H_5)_2O{\cdot}BH_2Cl$, and $(C_2H_5)O{\cdot}BHCl_2$. In the case of the BBr_3 reactions, products identified from their spectra include $H_3N{\cdot}BH_2Br$, $(C_2H_5)_2O{\cdot}BH_2Br$, and $(C_2H_5)_2O{\cdot}BHBr_2$ along with ether cleavage products. A hydrogen–halogen exchange mechanism appeared to account satisfactorily for the products of the BCl_3 and BBr_3 reactions. The only major products from the $H_3N{\cdot}BH_3$–BF_3 reactions were $H_3N{\cdot}BF_3$ and $(\mu\text{-}H_2N)B_2H_5$. An acid displacement followed by a hydrogen elimination mechanism is proposed for the BF_3 reaction.

Introduction

Although the compound has been known for some 20 years,[1,2] the chemistry of ammonia–borane is relatively undeveloped. Most of the known B-substituted derivatives of ammonia–borane are not prepared from the parent compound but rather by direct combination of ammonia with an appropriate borane. Probably the best characterized example is $H_3N{\cdot}BHF_2$, prepared from ammonia and difluoroborane.[3] On the basis of very early reports,[4,5] it is believed[6] that ammonia–*B*-chloroboranes are unstable with respect to ammonolysis of the boron–halogen bond. There is one report of $H_3N{\cdot}BH_2Cl$ as a decomposition product of $H_2B(NH_3)_2{}^+Cl^-$, but the adduct was not fully characterized.[7] In general, little is known about ammonia–*B*-haloboranes, their properties, or their stabilities.

The present investigation was undertaken to determine whether evidence could be obtained on the existence of B-halogenated ammonia–borane compounds. We wish to present such evidence obtained from a ^{11}B NMR investigation of the reaction of $H_3N{\cdot}BH_3$ with BF_3, BCl_3, and BBr_3.

Experimental Section

Ammonia–borane was prepared by methods described elsewhere.[8] Anhydrous BF_3 (Matheson) was used as obtained. Trichloroborane was purified by the method of Brown and Holmes[9] and stored in a glass vessel with a Teflon stopcock and O-ring joint. Tribromoborane was purified by distilling it from copper wool and storing in a glass vessel fitted with a Teflon stopcock and an O-ring joint, all covered with aluminum foil. Trifluoroborane ethyl etherate (Eastman) was used as obtained. Solvents, ethyl ether, tetrahydrofuran, and glyme (1,2-dimethoxyethane), were stirred, first with CaH_2 and then with $LiAlH_4$, and vapor transferred to glass storage vessels fitted with Teflon stopcocks and O-ring joints. Sodium tetrahydroborate was obtained with Callery Chemical Co. and used without purification.

Reactions were carried out by using a standard vacuum system[10] and NMR sample tubes were filled within a nitrogen-filled glovebox.[10] ^{11}B NMR spectra were obtained in the FT mode by using a Varian XL-100-15 spectrometer at 32.1 MHz with a Nicholet 1080 data system and a Nicholet MONA, wide band probe which could accommodate 12- or 18-mm sample tubes. Samples were held in 12-mm tubes fitted with a 5-mm coaxial tube containing $CDCl_3$ for locking purposes. Chemical shifts (δ) are given downfield from external $(C_2H_5)_2O{\cdot}BF_3$.

In a typical reaction, 3 mmol of $H_3N{\cdot}BH_3$ was placed in a 50-mL flask which was then attached to the vacuum line via a Teflon valve and a 9-mm O-ring joint. After evacuation, 30 mL of dry $(C_2H_5)_2O$ and the desired quantity of trihaloborane were condensed into the flask at −196 °C. The Teflon valve was then closed and the reaction mixture was stirred as it warmed to room temperature and was stirred for 18 h thereafter. The reaction vessel was then briefly opened to a vacuum line trap at −196 °C containing THF in order to flash away

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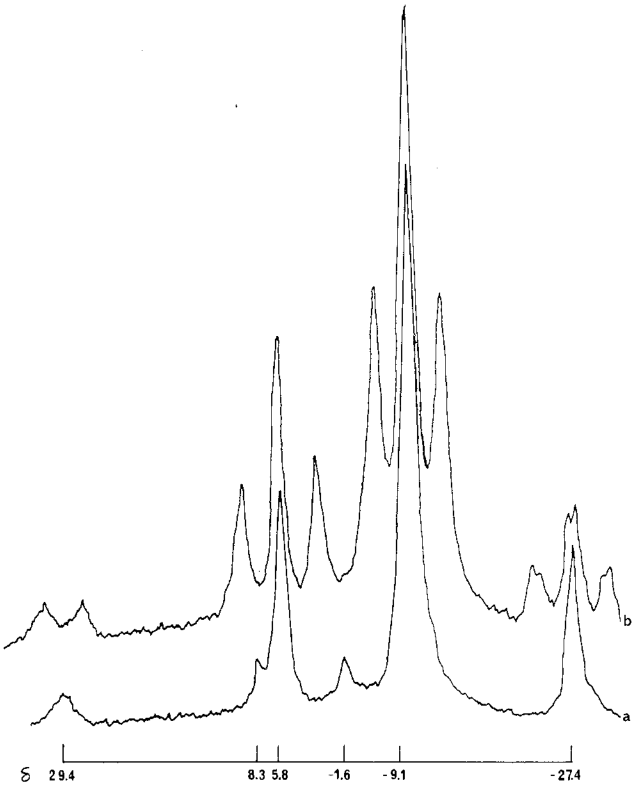


Figure 1. ^{11}B NMR spectrum of the 3:1 $H_3N{\cdot}BH_3$–BCl_3 reaction in ethyl ether: (a) proton decoupled, (b) proton coupled.

small quantities of gaseous B_2H_6 formed in some of the reactions. The vessel was then closed and removed to the glovebox where a sample for NMR analysis was removed. Unless otherwise noted, NMR spectra were obtained immediately (within 2 h) thereafter.

Results and Discussion

NMR Spectra. Ammonia–borane was reacted with BCl_3 in $(C_2H_5)_2O$ in 3:1, 2:1, and 1:2 molar ratios giving, in each case, slightly cloudy solutions. Such solutions could be stored at 0 °C for up to 2 weeks but evidenced a precipitate within a few days at 25 °C. The proton-decoupled ^{11}B NMR spectrum of a 3:1 $H_3N{\cdot}BH_3$–BCl_3 reaction mixture (Figure 1a) consisted of six singlets, δ 29.4 (5.6%), 8.3 (1.2%), 5.8 (16.8%), −1.6 (2.9%), −9.1 (60.3%), and −27.4 (13.2%). The proton-coupled spectrum (Figure 1b) contained a broad doublet, two triplets, and a 1:1:2:2:1:1 triplet of doublets. The doublet, centered at δ 29.4 (J_{BH} = 144 Hz), was tentatively assigned to borazine (lit.[11] δ 29.1, J_{BH} = 133 Hz). One triplet at δ 5.8 (J_{BH} = 135 Hz) represented $(C_2H_5)_2O{\cdot}BH_2Cl$ (lit.[12] δ 5.0 ± 0.3, J_{BH} = 136 Hz). The six-line multiplet at δ −27.4 appears to result from a triplet (J = 132 Hz), each component of which is split into a doublet (J = 27 Hz). This corresponds closely to the spectrum of μ-amino-diborane (lit.[13] δ −26.7, J_{BH} = 130 Hz, J_{BHB} = 30 Hz). The second triplet at δ −9.1 (J_{BH} = 120 Hz) is assigned to the new compound $H_3N{\cdot}BH_2Cl$. The δ 8.3 and −1.6 resonances do not appear in Figure 1b due to their small intensities and their proximity to larger peaks. They were tentatively assigned as representing $(C_2H_5)_2O{\cdot}BHCl_2$ and $H_3N{\cdot}BHCl_2$, respectively.

The proton-decoupled spectrum of the products of the 1:2 $H_3N{\cdot}BH_3$–BCl_3 reaction (Figure 2a) consisted of five resonances at δ 11.0 (2.9%), 8.4 (61.8%), 4.2 (6.2%), −1.3 (16.9%), and −8.9 (12.2%). The proton-coupled spectrum (Figure 2b) exhibited two singlets, two doublets, and a triplet. The singlet at δ 4.2 was found to represent $H_3N{\cdot}BCl_3$ by comparison with a sample of that compound prepared directly from NH_3 and BCl_3 in $(C_2H_5)_2O$. The doublet centered at δ 8.4 (J_{BH} = 166 Hz) was found to correspond to $(C_2H_5)_2O{\cdot}BHCl_2$ (lit.[14] δ 8.0 ± 0.2, J_{BH} = 163 Hz). The triplet at δ −8.9 was assigned to $H_3N{\cdot}BH_2Cl$ as noted above. The doublet centered at δ −1.3 (J_{BH} = 141 Hz) was assigned to the new compound $H_3N{\cdot}BHCl_2$.

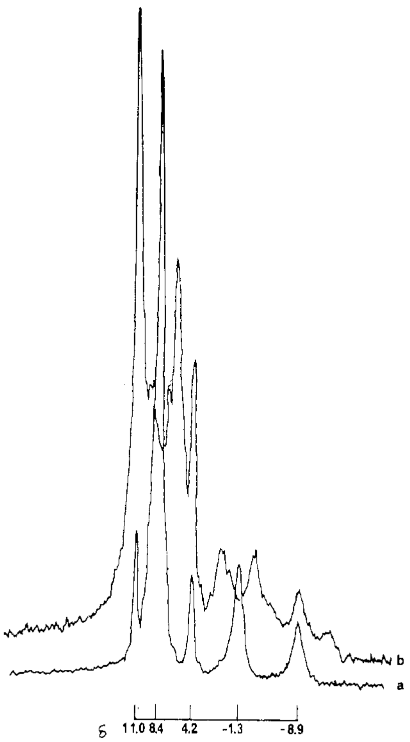


Figure 2. ^{11}B NMR spectrum of the 1:2 $H_3N{\cdot}BH_3$–BCl_3 reaction in ethyl ether: (a) proton decoupled, (b) proton coupled.

When the $H_3N{\cdot}BH_3$:BCl_3 ratio was 2:1, the ^{11}B spectrum of the resulting solution exhibited resonances at δ 30.8 (3.6%), 8.4 (16.0%), 5.8 (20.2%), 4.1 (trace), −1.3 (7.9%) and −9.1 (52.0%). These were assigned as borazine (or a derivative), $(C_2H_5)_2O{\cdot}BHCl_2$, $(C_2H_5)_2O{\cdot}BH_2Cl$, $H_3N{\cdot}BCl_3$, $H_3N{\cdot}BHCl_2$, and $H_3N{\cdot}BH_2Cl$, respectively.

The assignments for the two new compounds $H_3N{\cdot}BH_2Cl$ and $H_3N{\cdot}BHCl_2$ were made on the basis of their triplet and doublet multiplicities, establishing the number of borane hydrogens,[15,16] and on the values of the coupling constants. In the former compound the observed coupling constant, 120 Hz, compares closely with those reported for $(CH_3)_3N{\cdot}BH_2Cl$[17] (123 Hz) and $ClH_2B{\cdot}N(CH_3)_2CH_2CH_2N(CH_3)_2{\cdot}BH_2Cl$[18] (121 Hz). The coupling constant from the ^{11}B resonance of the latter compound, 141 Hz, compares reasonably well with the reported values for $(CH_3)_3N{\cdot}BHCl_2$[17] (148 ± 5 Hz). The observed chemical shifts are reasonable for $H_3N{\cdot}BH_2Cl$ and $H_3N{\cdot}BHCl_2$, being intermediate between those of $H_3N{\cdot}BH_3$ and $H_3N{\cdot}BCl_3$.

Reactions with stoichiometries of 2.8:1, 1:1, and 1:2 ($H_3N{\cdot}BH_3$–BBr_3) were carried out in $(C_2H_5)_2O$. The 1:2 $H_3N{\cdot}BH_3$–BBr_3 reaction produced a clear solution with ^{11}B resonances occurring at δ 27.3 (4.5%), 22.1 (14.4%), 18.0 (26.2%), 0.4 (trace), 0.3 (18.4%), and −12.1 (36.4%) (Figure 3a). The resonance at δ −12.1 appeared as a triplet (J_{BH} = 126 Hz) in the proton-coupled spectrum (Figure 3b) representing the new compound $H_3N{\cdot}BH_2Br$. A doublet centered at δ 0.3 (J_{BH} = 165 Hz) was believed to represent $(C_2H_5)_2O{\cdot}BHBr_2$. Another doublet at δ 27.3 (J_{BH} = 161 Hz) was tentatively assigned as representing $(C_2H_5O)_2BH$ (lit.[19] $(CH_3O)_2BH$ δ 26.1, J_{BH} = 141 Hz). Singlets at δ 22.1, 18.0, and 0.4 were essentially identical with those in the ^{11}B NMR spectrum of $(C_2H_5)_2O{\cdot}BBr_3$ in $(C_2H_5)_2O$ after 24 h at 25 °C. However, none of these represents $(C_2H_5)_2O{\cdot}BBr_3$ itself which, when freshly prepared, exhibits a singlet at δ −5.8 (lit.[20] δ −6.1). The resonance at

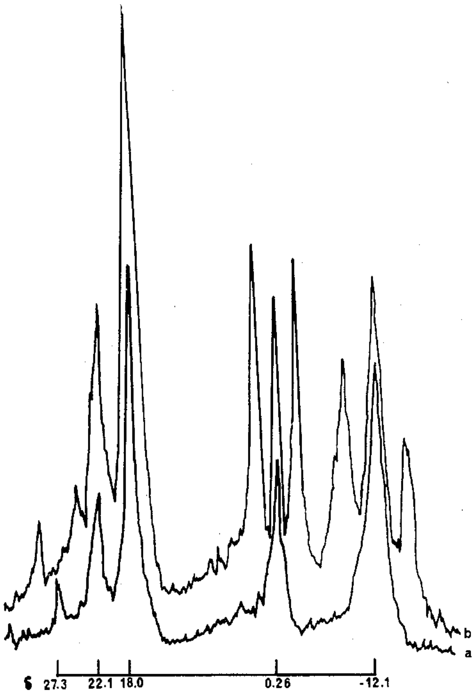


Figure 3. ^{11}B NMR spectrum of the 1:2 $H_3N{\cdot}BH_3$–BBr_3 reaction in ethyl ether: (a) proton decoupled, (b) proton coupled.

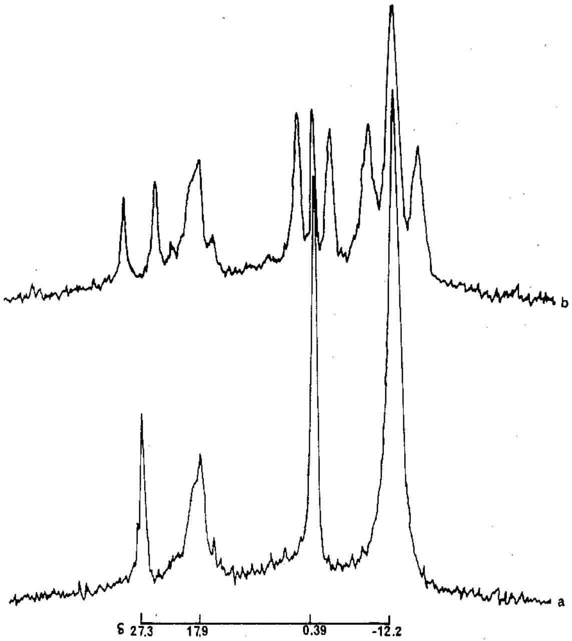


Figure 4. ^{11}B NMR spectrum of the 1:1 $H_3N{\cdot}BH_3$–BBr_3 reaction in ethyl ether: (a) proton decoupled, (b) proton coupled.

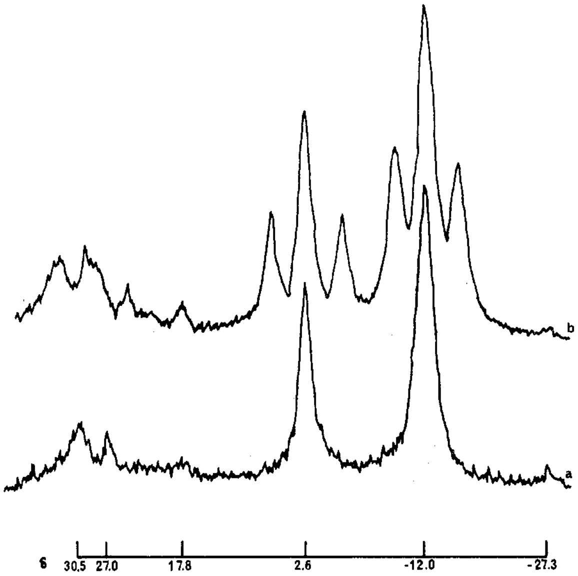


Figure 5. ^{11}B NMR spectrum of the 2.8:1 $H_3N{\cdot}BH_3$–BBr_3 reaction in ethyl ether: (a) proton decoupled, (b) proton coupled.

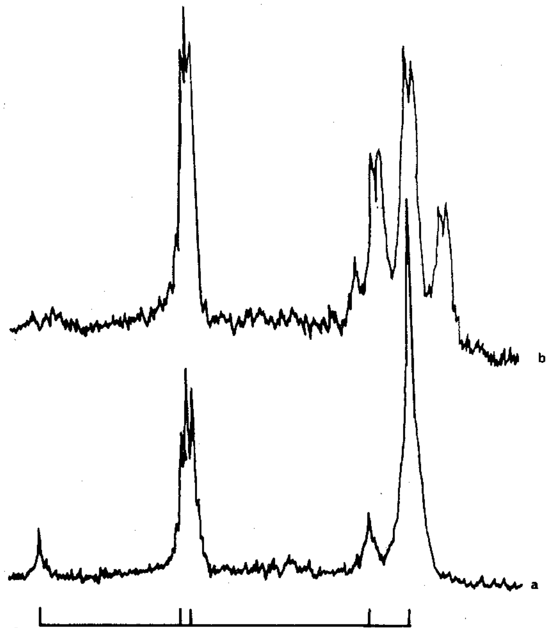


Figure 6. ^{11}B NMR spectrum of the 2:1 $H_3N{\cdot}BH_3$–BF_3 reaction in ethyl ether: (a) proton decoupled, (b) proton coupled.

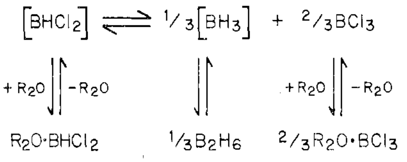
δ 18.0 can be attributed to triethyl borate (lit.[21] δ 18.1) but the remaining resonances were not identified.

The proton-decoupled ^{11}B spectrum of the slightly cloudy solution from the 1:1 $H_3N{\cdot}BH_3$–BBr_3 reaction (Figure 4a) closely resembled that described for the 1:2 reaction but with different relative intensities: δ 27.3 (5.9%), 17.9 (17.5%), 0.41 (4.6%), 0.39 (17.5%), and −12.2 (54.5%). Figure 4b shows the proton-coupled spectrum of the same sample.

A somewhat cloudy solution resulted from the 2.8:1 $H_3N{\cdot}BH_3$–BBr_3 reaction. The proton-decoupled ^{11}B spectrum (Figure 5a) of the clear supernatant liquid exhibited resonances at δ 30.5 (15.4%), 27.0 (6.9%), 17.8 (4.4%), 2.6 (22.7%), −12.0 (48.6%), and −27.3 (2.1%). The proton-coupled spectrum (Figure 5b) evidenced a broad doublet ($J_{BH} \simeq 124$ Hz) centered at δ 30.5 which may represent borazine[11] but was not further investigated. The triplet ($J_{BH} = 137$ Hz) centered at δ 2.6 was attributed to $(C_2H_5)_2O{\cdot}BH_2Br$. The doublet ($J_{BH} = 162$) at δ 27, the broad singlet at δ 17.8, the triplet ($J_{BH} = 124$ Hz) at δ −12.0, and the resonance at δ −27.4, as described previously, indicated the presence of $(C_2H_5O)_2BH$, $(C_2H_5O)_3B$, $H_3N{\cdot}BH_2Br$, and $H_2NB_2H_5$, respectively.

Ammonia–borane was combined with BF_3 in several stoichiometries with both ethyl ether and glyme (1,2-dimethoxyethane) as solvents, yielding slightly cloudy solutions in all cases. Typical ^{11}B spectra are shown in Figure 6 for the 2:1 $H_3N{\cdot}BH_3$–BF_3 reaction in ethyl ether. The 1:1:2:2:1:1 triplet of doublets centered at δ −27.3 represents $(\mu\text{-}H_2N)B_2H_5$ (lit.[13] δ −26.7) with observed coupling constants $J_{BH} = 131$ Hz and $J_{BHB} = 31$ Hz (lit.[13] $J_{BH} = 130$ Hz, $J_{BHB} = 30$ Hz). In the proton-decoupled spectrum (Figure 6a) the singlet at δ −22.2 is due to unreacted $H_3N{\cdot}BH_3$ and the multiplet at δ −0.74 ($J_{BF} \simeq 14.7$ Hz) arises from $H_3N{\cdot}BF_3$ (lit.[15] δ −1.1, $J_{BF} = 13.9$ Hz). The overlapping singlet (δ 0.27) results from residual $(C_2H_5)_2O{\cdot}BF_3$. Another small singlet, visible in Figure 6a at δ

Scheme I[a]



17.7, is believed to represent B_2H_6 (lit.[22] δ 17.6).

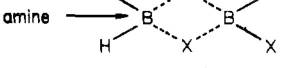
The maximum yield of $(\mu\text{-}H_2N)B_2H_5$ was 60–80% obtained in reactions with 2:1 $H_3N{\cdot}BH_3{:}BF_3$ ratios. The yield was determined from integrated areas of NMR spectra and checked by measuring the quantity of H_2 gas produced in the reactions on the vacuum line. Attempts to isolate pure $(\mu\text{-}H_2N)B_2H_5$ from the reaction mixtures were not successful. When the reaction mixture (ether solvent) was held at 0 °C and fractionated through traps held at −45, −65, −78 and −196 °C, $(\mu\text{-}H_2N)B_2H_5$ appeared to concentrate for a while in the −65 °C trap but gradually transferred to the −78 °C trap where it was held with ethyl ether. A gas-phase IR spectrum sampled from the −65 °C trap during the fractionation showed bands as follows (cm^{-1}): 3515 (w), 2575 (s), 2500 (m), 1670 (m), 1015 (ms) and 995 (m) along with characteristic bands of $(C_2H_5)_2O$. The bands at 2575 and 2500 cm^{-1} seem to correspond to those of the BH_2 groups of $(\mu\text{-}(CH_3)_2N)B_2H_5$ which are reported[23] at 2550 and 2480 cm^{-1}, while the band at 1670 cm^{-1} closely resembled that believed to represent the bridge hydrogen in $(\mu\text{-}(CH_3)_2N)B_2H_5$ at 1635 cm^{-1}. From band intensities, it was estimated that the gas mixture contained roughly a 50:50 mixture of $(\mu\text{-}H_2N)B_2H_5$ and $(C_2H_5)_2O$.

The reaction was repeated in glyme in an attempt to isolate pure $(\mu\text{-}H_2N)B_2H_5$, but the reaction occurred more slowly and, again, the fractionation was unsuccessful. If a method were available for separation of the μ-amino-diborane from the solvent, the 2:1 $H_3N{\cdot}BH_3\text{–}BF_3$ reaction would constitute an effective synthetic method for μ-amino-diborane.

In an attempt to drive the reaction to consume all the ammonia–borane, a reaction was carried out with a slight excess of trifluoroborane (1.8:1 $H_3N{\cdot}BH_3\text{–}BF_3$) in ethyl ether for a longer period (40 h). Hydrogen gas was removed periodically by cooling the reaction mixture to −196 °C and opening the reaction vessel to the pump through a U-trap held at −196 °C. Any condensables collected in the trap were returned to the reaction vessel. The ^{11}B NMR spectrum revealed that small quantities of starting materials were still present after 40 h along with what appeared to be ether cleavage products at δ 27.3 (J_{BH} = 161.5 Hz) and δ 18.1 (br, s).

Reactions of Ammonia–Borane with Trichloroborane. The solubility of ammonia–borane in solvents of low polarity is very limited, resulting in the use of ether solvents in this investigation. This requirement led to the complication that ether cleavage occurred in reactions where BCl_3, BBr_3, or B_2H_6 were present in solution at 25 °C for any appreciable length of time.

B-Halogenation of amine–boranes with trihaloboranes was reported earlier by Nöth and Beyer[24] although ammonia–borane was not included. The hydrogen–halogen exchange reactions were believed by those investigators to proceed through a mechanism involving a four-center transition state:



If such a mechanism were operative in the presence of a donor solvent such as ethyl ether, the reaction between ammonia–borane and trichloroborane would be expected to produce ammonia–chloroborane and dichloroborane

$$H_3N{\cdot}BH_3 + BCl_3 \rightarrow H_3N{\cdot}BH_2Cl + [BHCl_2]$$

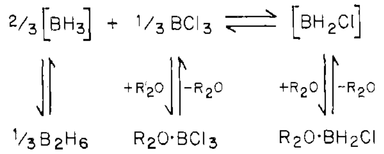
which, as shown in Scheme I, may form an etherate complex or disproportionate. It is probable that the etherates of BCl_3 and $BHCl_2$ are subject to some degree of dissociation although Brown and Tierney[25] demonstrated that in the latter case the equilibrium lies predominantly toward $(C_2H_5)_2O{\cdot}BHCl_2$. The disproportionation of free $BHCl_2$ appears to require dimeric intermediates perhaps of the type proposed by Myers and Putnam,[26] but their specific nature is not critical to these considerations.

Table I. Summary of Product Yields of $H_3N{\cdot}BH_3\text{–}BCl_3$ Reactions[a]

	$H_3N{\cdot}BH_3{:}BCl_3$ ratio		
product	3:1	2:1	1:2
$H_3N{\cdot}BH_2Cl$	60.3	52.0	12.2
$H_3N{\cdot}BHCl_2$	2.9	7.9	16.9
$H_3N{\cdot}BCl_3$		trace	6.2
$(C_2H_5)_2O{\cdot}BH_2Cl$	16.8	20.2	
$(C_2H_5)_2O{\cdot}BHCl_2$	1.2	16.0	61.8
$(C_2H_5)_2O{\cdot}BCl_3$			2.9
$(\mu\text{-}H_2N)B_2H_5$	13.2		
$H_3B_3N_3H_3$(?)	6.5	3.6	

[a] Relative percent of observed boron-containing products by integration of ^{11}B resonances.

Scheme II[a]



The formation of BCl_3 in the disproportionation complicates the stoichiometric relationships in the chlorination reaction. Treatment of 1 mol of $H_3N{\cdot}BH_3$ with 1 mol of BCl_3 could produce 1 mol of $H_3N{\cdot}BH_2Cl$ and 1 mol of dichloroborane etherate which, upon partial disproportionation, yields additional BCl_3 which chlorinates more $H_3N{\cdot}BH_3$, if available, or, if not, could effect dichlorination:

$$H_3N{\cdot}BH_2Cl + BCl_3 \rightarrow H_3N{\cdot}BHCl_2 + [BHCl_2]$$

Another source of trihaloborane consumption is ether cleavage reactions, presumably of etherate complexes, the final products of which are alkyl borates.[27] The degree of ether cleavage was minor in BCl_3 reactions but considerably more important in BBr_3 reactions. It is also possible that ether cleavage occurs in the presence of B_2H_6. The degree to which ether cleavage occurs depends on the concentration of the etherates and the length of time they reside in solution at room temperature.

The numerous equilibria and competing reactions involved in these halogenation reactions make a detailed analysis of the yields impractical. We may observe, however, that the yields (based on peak area) of $H_3N{\cdot}BH_2Cl$ (Table I) decreased as the relative amount of BCl_3 increased and that the reverse was true for $H_3N{\cdot}BHCl_2$, which appeared in smaller overall yields. The reactivity of amine–boranes toward chlorinating agents is known[18,28] to decrease as the number of chlorines on boron increases, accounting for the lower yields of $H_3N{\cdot}BHCl_2$ and $H_3N{\cdot}BCl_3$, which were formed in appreciable amounts only when excess BCl_3 was present. As can be seen from Table I, about two-thirds of the $H_3N{\cdot}BH_3$ was converted to $H_3N{\cdot}BHCl_2$ and $H_3N{\cdot}BCl_3$ in the 1:2 reaction.

In reactions with more than 1 mol of $H_3N{\cdot}BH_3$/mol of BCl_3, after the initial reaction to produce $H_3N{\cdot}BH_2Cl$, the unreacted $H_3N{\cdot}BH_3$ may react with BCl_3 from the disproportionation of $BHCl_2$ (Scheme I), yielding additional $H_3N{\cdot}BH_2Cl$ and shifting the disproportionation equilibrium away from $[BHCl_2]$, producing more B_2H_6. The increasing B_2H_6 concentration favors the formation of monochloroborane etherate via Scheme II. This accounts for the presence of that product in the 3:1 and 2:1 reactions (Table I).

Table II. Summary of Product Yields of $H_3N\cdot BH_3$–BBr_3 Reactions[a]

	$H_3N\cdot BH_3$:BBr_3 ratio		
product	2.8:1	1:1	1:2
$H_3N\cdot BH_2Br$	48.6	54.5	36.4
$(C_2H_5)_2O\cdot BH_2Br$	22.7		
$(C_2H_5)_2O\cdot BHBr_2$		17.5	18.4
$(C_2H_5O)_3B$ plus other ether cleavage products	4.1	22.1	40.6
$(C_2H_5O)_2BH$	6.9	5.9	4.5
$H_3B_3N_3H_3$(?)	15.4		
$(\mu\text{-}H_2N)B_2H_5$	2.1		

[a] Relative percent of observed boron-containing products by integration of ^{11}B resonances.

As the B_2H_6 concentration increases, under circumstances where excess $H_3N\cdot BH_3$ is present, the competing reaction

$$H_3N\cdot BH_3 + {}^1/_2B_2H_6 \xrightarrow{R_2O} (\mu\text{-}H_2N)B_2H_5 + H_2$$

may occur. The aminodiborane product was observed only in the 3:1 reactions. This reaction is discussed in more detail in connection with $H_3N\cdot BH_3$–BF_3 reactions.

The presence of borazine or a derivative thereof in the 3:1 and 2:1 reactions presumably arises from hydrogen or hydrogen halide elimination from $H_3N\cdot BH_2Cl$ or $H_3N\cdot BHCl_2$ since $H_3N\cdot BH_3$ itself does not give borazine under these conditions. The fact that no borazine was observed in the 1:2 reaction may indicate that excess $H_3N\cdot BH_3$ (or B_2H_6) may play a necessary role in its formation.

Reactions of Ammonia–Borane with Boron Tribromide. Hydrogen–halogen exchange was also observed in $H_3N\cdot BH_3$–BBr_3 reactions effecting the synthesis of the new compound $H_3N\cdot BH_2Br$. The dibromo derivative was not produced, perhaps owing to the deactivation of the monobromo derivative by the halogen. Also, tribromoborane is considered to be a stronger ether cleavage agent than trichloroborane[29] so that some BBr_3 is consumed through ether cleavage. The presence of significant amounts of ether cleavage products in the reaction mixture, particularly in the BBr_3-rich reactions, confirms the loss of tribromoborane by this side reaction. The apparent yields of $H_3N\cdot BH_2Br$ follow the same pattern as for the monochloro compound except that the formation of an unusually large amount of borazine or related compound in the 2.8:1 reaction reduced the yield of ammonia–monobromoborane in that reaction (Table II). No borazine was observed in the 1:1 and 1:2 stoichiometries. The same mechanistic steps as proposed for the BCl_3 reactions appear to account satisfactorily for the products of the BBr_3 reactions. The bromoborane etherates, $(C_2H_5)_2O\cdot BH_2Br$ and $(C_2H_5)_2O\cdot BHBr_2$, are new compounds identified by the multiplicites of their ^{11}B signals and the close similarities of their B–H coupling constants to those of the better known chloroborane etherates. Similarly, the B–H coupling constant of $H_3N\cdot BH_2Br$, 126 Hz, is nearly identical with that of $(CH_3)_3N\cdot BH_2Br$, 125 Hz,[30] confirming that assignment.

Reactions of Ammonia–Borane with Trifluoroborane. Hydrogen–fluorine exchange was not observed in any of the reactions carried out between $H_3N\cdot BH_3$ and BF_3 in ether or glyme solution. The major products were μ-amino-diborane and $H_3N\cdot BF_3$, judging from their ^{11}B NMR spectra, and H_2 was also produced. The yield of products was maximized at a 2:1 $H_3N\cdot BH_3$–BF_3 ratio, suggesting that the reaction may be represented as

$$2(H_3N\cdot BH_3) + BF_3 \xrightarrow[25\ ^\circ C]{(C_2H_5)_2O} (\mu\text{-}H_2N)B_2H_5 + H_3N\cdot BF_3 + H_2$$

Even when an excess of BF_3 was employed and the reaction mixture was stirred 40 h at 25 °C instead of 18 h, the reaction failed to reach completion as evidenced by small peaks in the ^{11}B NMR spectrum indicative of $H_3N\cdot BH_3$ and $(C_2H_5)_2O\cdot BF_3$.

In what appears to be an analogous reaction, Nöth and Beyer[24] combined dimethylamine–borane with BF_3 at 120 °C, producing μ-(dimethylamino)-diborane. The bridged aminodiborane product was identified by its ^{11}B NMR spectrum[13] and its infrared spectrum although it was never completely separated from solvent.

Since BF_3 apparently displaces $[BH_3]$ from trimethylamine–borane,[24] forming B_2H_6, it is quite possible that a similar reaction occurs with ammonia–borane:

$$H_3N\cdot BH_3 + BF_3 \rightarrow H_3N\cdot BF_3 + {}^1/_2B_2H_6$$

Small quantities of diborane were identified by ^{11}B NMR as products of the 2:1 $H_3N\cdot BH_3$–BF_3 reaction and another reaction where the ratio was between 2:1 and 1:1. The diborane formed in the acid displacement step combines with the remaining ammonia–borane to produce the μ-amino-diborane:

$$H_3N\cdot BH_3 + {}^1/_2B_2H_6 \rightarrow (\mu\text{-}H_2N)B_2H_5 + H_2$$

In fact, this reaction was observed by earlier workers[31] investigating the chemical properties of ammonia–borane. Ether cleavage products, presumably resulting from the presence of free diborane, were also noted among the products.

Acknowledgment. The authors gratefully acknowledge the U.S. Department of Energy and The Robert A. Welch Foundation under Grant E-439 for support of this investigation.

Registry No. $H_3N\cdot BH_3$, 43054-26-8; BCl_3, 10294-34-5; BBr_3, 10294-33-4; BF_3, 7637-07-2; $H_3N\cdot BH_2Cl$, 71648-05-0; $H_3N\cdot BHCl_2$, 71648-06-1; $H_3N\cdot BCl_3$, 49860-18-6; $(C_2H_5)_2O\cdot BH_2Cl$, 36594-41-9; $(C_2H_5)_2O\cdot BHCl_2$, 41156-66-5; $(C_2H_5)_2O\cdot BCl_3$, 2102-03-6; $(\mu\text{-}H_2N)B_2H_5$, 39046-41-8; $H_3N\cdot BH_2Br$, 71648-07-2; $(C_2H_5)_2O\cdot BH_2Br$, 69765-80-6; $(C_2H_5)_2O\cdot BHBr_2$, 71648-08-3; $(C_2H_5O)_3B$, 150-46-9; $(C_2H_5O)_2BH$, 23561-28-6; $H_3N\cdot BF_3$, 15433-37-1.

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